SOME CHARACTERISTICS OF EVAPORATED ELECTROLUMINESCENT PHOSPHOR FILMS

TECHNICAL DOCUMENTARY REPORT NO. ESD-TDR-63-169

May 1963

J. V. Hirsch

Prepared for

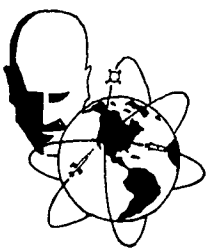
DIRECTORATE OF RADAR AND OPTICS

ELECTRONIC SYSTEMS DIVISION

AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

L. G. Hanscom Field, Bedford, Massachusetts



Prepared by

THE MITRE CORPORATION
Bedford, Massachusetts
Contract AF33(600)-39852 Project 708

ABSTRACT

Vacuum deposited electroluminescent phosphor light sources have characteristics radically different from conventional electroluminescent panels. This paper describes the fabrication and some characteristics of films composed of yellow (ZnS:Mn;Cl) and green (ZnS:Cu,Pb;Cl) phosphors. Among the properties studied are brightness levels, spectral distribution and resistance and capacitance measurements.

INTRODUCTION

Recently, a new approach to the fabrication of electro-luminescent,*[1] (EL), phosphors has given impetus to the development of solid state devices for lighting, display and opto-logical applications.[2] It turns out that if the EL phosphor is vacuum deposited, the brightness levels obtained for a given voltage across the phosphor are several orders of magnitude greater than previously obtainable. Moreover, a d-c field can also produce luminescence; with "bulk" panels, i.e., the phosphor powder is imbedded in a dielectric material, d-c excitation is impossible.

This paper is intended to describe the methods of fabrication of thin EL films and some of the reproducible characteristics of the films. The characteristics which have been studied are those which would be useful in applications to display or opto-logical devices. Included are brightness levels, spectral distribution and resistance and capacitance measurements.

FABRICATION OF THIN E-L FILMS

The host material used in most of the EL work is zinc sulphide (ZnS), a well known phosphor material. To the host material are added various activative materials, either singly or multiply; copper, manganese and silver are the most common. In addition a co-activator is required for compensation;[3] chlorene is the most common coactivator. It is the presence of the activator and coactivator in the host crystal that gives rise to luminescence centers. The process

---

* Electroluminescence as used here refers to the generation of visible light by means of an electric field.

of activation is carried out at elevated temperatures where the diffusion of the activator and coactivator into the host crystal can readily proceed.

In making thin film E-L phosphors, the concentrations of activators and coactivators are disturbed due to a fractional vaporization of the phosphor components; the coactivator is almost entirely lost. So the problem of producing phosphor films is one of reactivating the host material. There are several schemes for doing this.

1. The phosphor film can be made at the hot substrate in vacuum by evaporating pure ZnS with activator and co-activator salts in the proper ratio to allow for the different evaporation rates.
2. The phosphor can be normally evaporated and the film subsequently heated in the presence of vaporized activator and coactivator salts.
3. The phosphor can be normally evaporated and the film subsequently imbedded in finely divided bulk phosphor at elevated temperatures.

The last process is due to W. A. Thornton[4] and is most satisfactory because the bulk phosphor has the exact concentrations of activator and coactivator required. In this manner yellow (ZnS: Mn;Cl) and to some extent green (ZnS:Cu,Pb;Cl) phosphor films have been made at MITRE.

The phosphor film samples were deposited on one inch square substrates of Corning #7280 glass. The special glass was required in order to match the thermal coefficient of expansion of ZnS at activation temperatures. Otherwise adherence problems would arise with films thicker than 1.5 microns (μ). The glass substrates were pre-coated with tin oxide (EC layer). The EC layers were electrically conducting (resistivity of 50-100 ohms per square) and were transparent (80%). The phosphor was deposited over a 3/4 inch square centered on the substrate. For the evaporation a resistance-heated molybdenum "V" boat was used. The evaporation temperature was about 1250°C giving deposition rates of about 15 Å per second. The phosphor film thickness was about 1.4-1.6μ as determined by interference fringes. After deposition the substrates were imbedded in finely divided bulk phosphor and heated to 710°C for 15 minutes in an inert atmosphere. Next a deposition of silicon monoxide was made over the entire phosphor square. The thickness of this insulating layer was varied from sample to sample in the range of 100Å to 1000Å. The insulating layer inhibited voltage breakdown of the phosphor film. Finally a pattern of nine aluminum dots 5/32 of an inch in diameter were deposited over the silicon monoxide layer. The vapor depositions mentioned were done at pressures around 10^{-5} Torr. A phosphor film sample as described is shown schematically in Figure 1.

CHARACTERISTICS

1. Voltage Brightness

In Figure 2 the brightness versus a-c voltage data for a ZnS:Mn;Cl film with a .1μ layer of silicon monoxide are plotted. The effect of the insulating layer is to reduce the d-c luminescence; the

a-c luminescence is not appreciably affected. When the thickness of silicon monoxide reaches .1μ the d-c response is reduced by a factor of 30. The interesting point is that the brightness of the films varies as $\exp(aV)$ at the higher voltages. At lower voltages there is a deviation toward an $\exp(b/V)$ dependence. Bulk panels have a brightness dependence of $\exp(c/V^2)$. If one thinks of incorporating an EL film in an X-Y grid structure, a built in ratio of brightness at full to half voltage of at least 133 is available. With bulk panels the corresponding ratio would be about 5. A frequency dependence of brightness is also noted. In all cases the frequency dependence is almost linear being slightly super linear. This also can be correlated with the presence of the silicon monoxide layer. It turns out that if $RC \ll \frac{1}{\omega}$ where C is the capacitance of the silicon monoxide layer and ω is the radial frequency of exciting voltage, the variation of brightness with frequency is super linear.[5]

Figure 3 shows the brightness dependence of the same sample on d-c voltage. The effect on the magnitude of brightness of the silicon monoxide layer can clearly be seen. Without a silicon monoxide layer brightnesses comparable to a-c excitation were observed. Unfortunately these samples proved to be unstable. With improved fabrication techniques this can be significantly improved. The d-c luminescence also has an exponential dependence on voltage. The corresponding d-c current is exponential but does not parallel the brightness curve. However, this may be due to leakage current.

Figure 4 shows the dependence of brightness an a-c voltage for green ZnS:Cu,Pb;Cl films. It should be mentioned here that the activation process for the green phosphor films is not as straightforward as

for the yellow. The yellow phosphor is not too sensitive to the concentration of activator material and consequently activation times and temperatures are not critical; just the opposite is true for the green phosphor. As a result higher heat treating temperatures were used for the green phosphor films to assure activation from the bulk phosphor. The higher temperatures caused an increase in the resistivity of the EC layer of a factor of 100. This essentially introduced a large resistance in series with the phosphor film and reduced the voltage across the phosphor. Figure 4 clearly shows low brightnesses for relatively high voltage and an exp(c/V) dependence which is characteristic of phosphor films at low voltages. For these reasons no d-c luminescence of the green films was observed.

2. Spectral Distribution

Figure 5 is a plot of the spectral distribution of yellow (ZnS:Mn;Cl) and green (ZnS:Cu,Pb;Cl) phosphor films. The yellow film was excited with 20 kcps voltage and the green with 20 and 10 kcps voltage. The distribution is quite narrow for the yellow phosphor being 56 mμ wide at the half-amplitude points. The peak occurs at 571 mμ. The green phosphor film has two peaks. One is in the blue region and the other is in the green region. At low frequencies the green is dominant and the film appears green. As the frequency is increased the blue component becomes more and more prominent and the film appears almost blue. This phenomenon is nothing new and is believed to be a result of the interaction of blue and green centers in the phosphor after excitation but prior to luminescence.[6]

3. Resistance and Capacitance

The capacitance of the films was found to range from .0009μf to .0012μf and did not change appreciably when the films were luminescencing. The capacitance was more uniform than the 30% figure just given if only cells on the same sample are considered, in which case the spread of values is about 10%. Since the capacitance is essentially constant during luminescence it may be expected that the capacitance of a cell arises from the phosphor and the silicon monoxide layer. The relative dielectric constant of ZnS is about 7.2, that of silicon monoxide 4. The average dielectric constant of the sample layer would be 7. With a capacitance of .001μf the layer thickness is:

$$t = \epsilon_o \epsilon_r \frac{A}{C} = \frac{8.85 \times 10^{-12} \times 7 \times 1.8 \times 10^{-5}}{10^{-9}} = 1.10 \times 10^{-6} \text{ meters}$$

or t = 1.1 microns.

This compares favorably with the observed thickness.

The resistance of the films from the aluminum to the E-C layer was about 10 megohms when measured at low voltage with a point probe. However when the films were emitting light a dynamic resistance of about 1,500 ohms was observed. If the capacitance of the silicon monoxide is taken to be .00007μf the RC time constant would be about 10^{-7} second. For 20 kcps, $1/\omega$ is about 8×10^{-6} second. This would serve to confirm the slightly superlinearity of the frequency dependence.

DISCUSSION

From the work already completed it is evident that high-resolution, the bright light sources for display or opto-logical devices can be realized with EL phosphor films. Also indicated, is the fact that reproducibility, uniformity and performance can be improved with better fabrication techniques including a closely controllable environment. For example, the luminous efficiency of the films described is about .2 lumens per watt. If the EC layers used were adequately matched to the heat treating cycle power consumption could be reduced by a factor of 4 and still higher brightness could be attained at lower voltage. These considerations are not speculative, they can be implemented, by and large, with existing facilities save for the need of an ultra-clean environment.

Some preliminary work has just begun on pulse excitation of the phosphor films. It appears that the yellow phosphor has a prohibitively long decay time for most device applications. The green phosphor is polarity sensitive to pulses. In one mode on to off times of the light output of 5μ seconds were noted. In the other mode with slightly less light output on to off times of .8μ second have been observed.

Future work will be concerned with further pulse excitation studies and the problems associated with making small, planar arrays of EL elements.

James V. Hirsch

JH:tjm

James V. Hirsch

BIBLIOGRAPHY

1. For a dated but comprehensive idea of the application of EL see H. F. Ivey, "Recent Advances in Luminescence", PGCP, Dec. 1957
2. W. A. Thornton, Jour. Appl. Phys. pp 123, 1959 (Letter)
3. W. W. Piper and F. E. Williams - Solid State Physics Vol. 6, pp. 111.
4. W. A. Thornton- "Method of Forming Films of Electroluminescent Phosphor", United States Patent #3,044,902, July 17, 1962.
5. P. Zalm, "Electroluminescence of ZnS Type Phosphors", Philips Research Reports Vol. 11, No.6, pp. 436 1956
6. Ibid

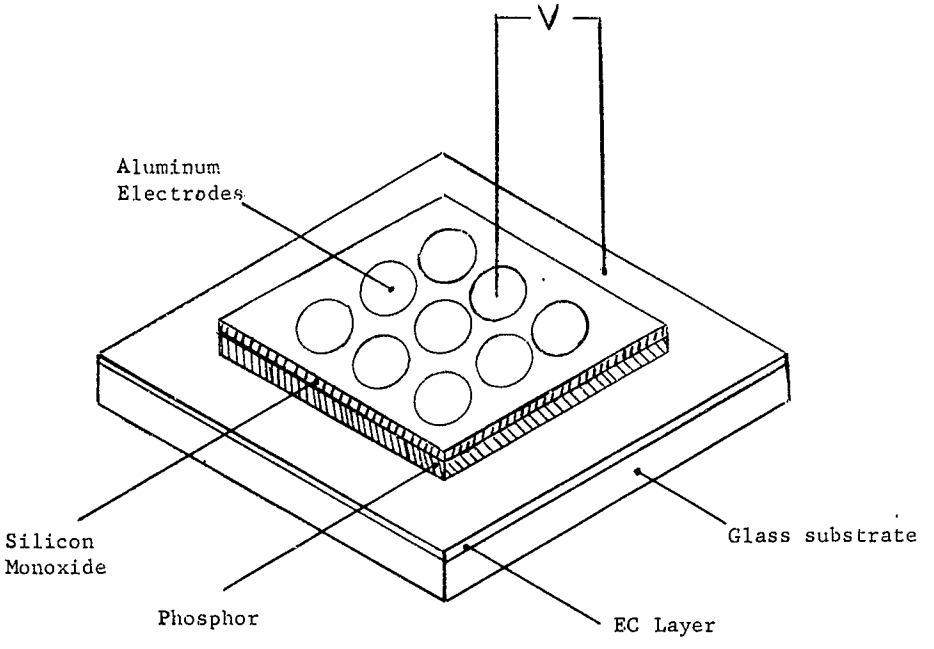


Figure 1

Schematic of an EL Phosphor Film Sample

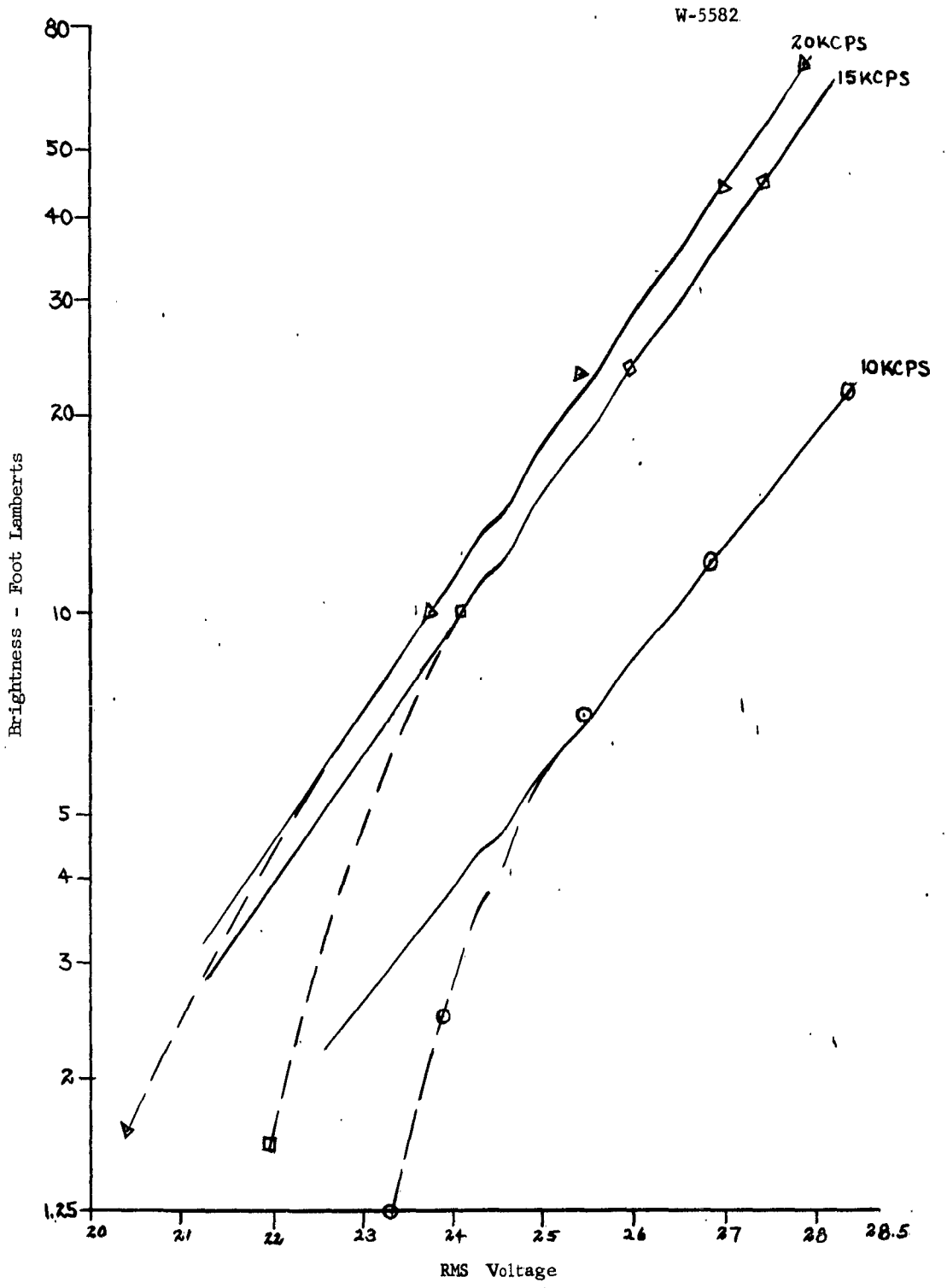

W-5582
20KCPS
15KCPS
10KCPS
80
50
40
30
20
10
5
4
3
2
1.25
Brightness - Foot Lamberts
20
21
22
23
24
25
26
27
28
28.5
RMS Voltage

Figure 2

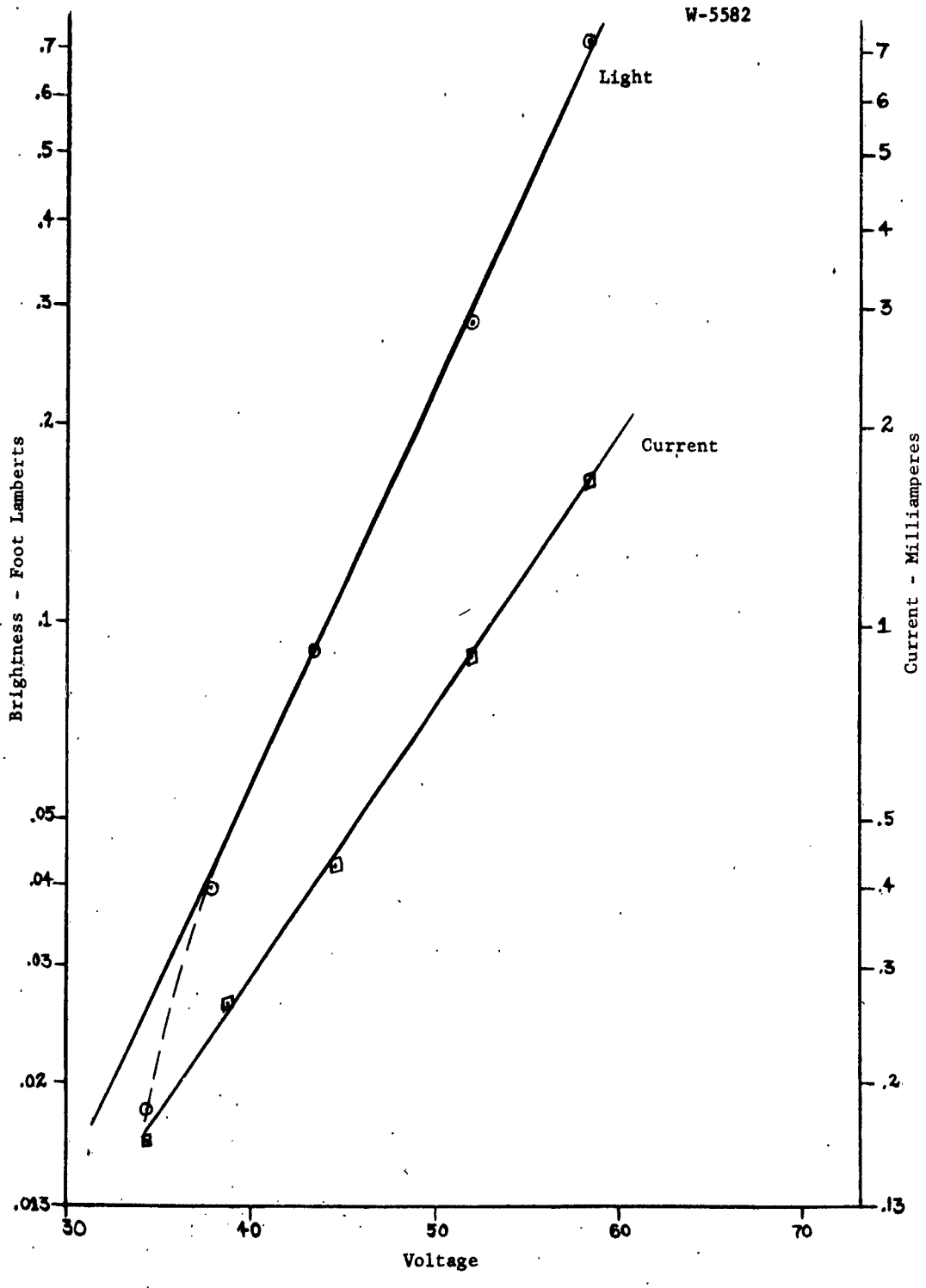


Figure 3

DC Voltage - Current Brightness Characteristic for a ZnS:Mn;Cl film 1.5μ thick with .1μ silicon monoxide

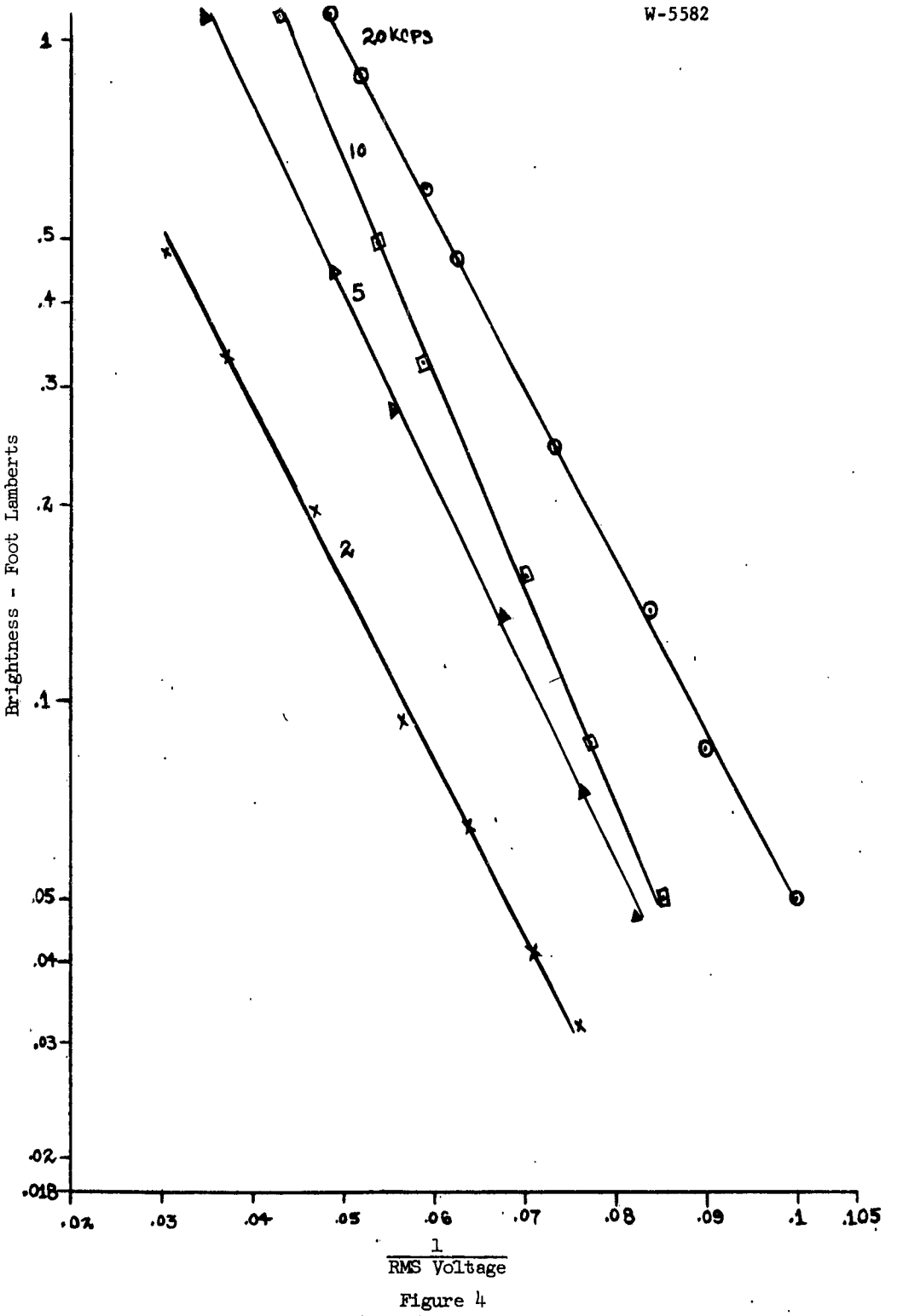


Figure 4

VOLTAGE-BRIGHTNESS CHARACTERISTIC For a ZnS:Cu, Pb;Cl film 1.5μ thick with .1μ silicon monoxide

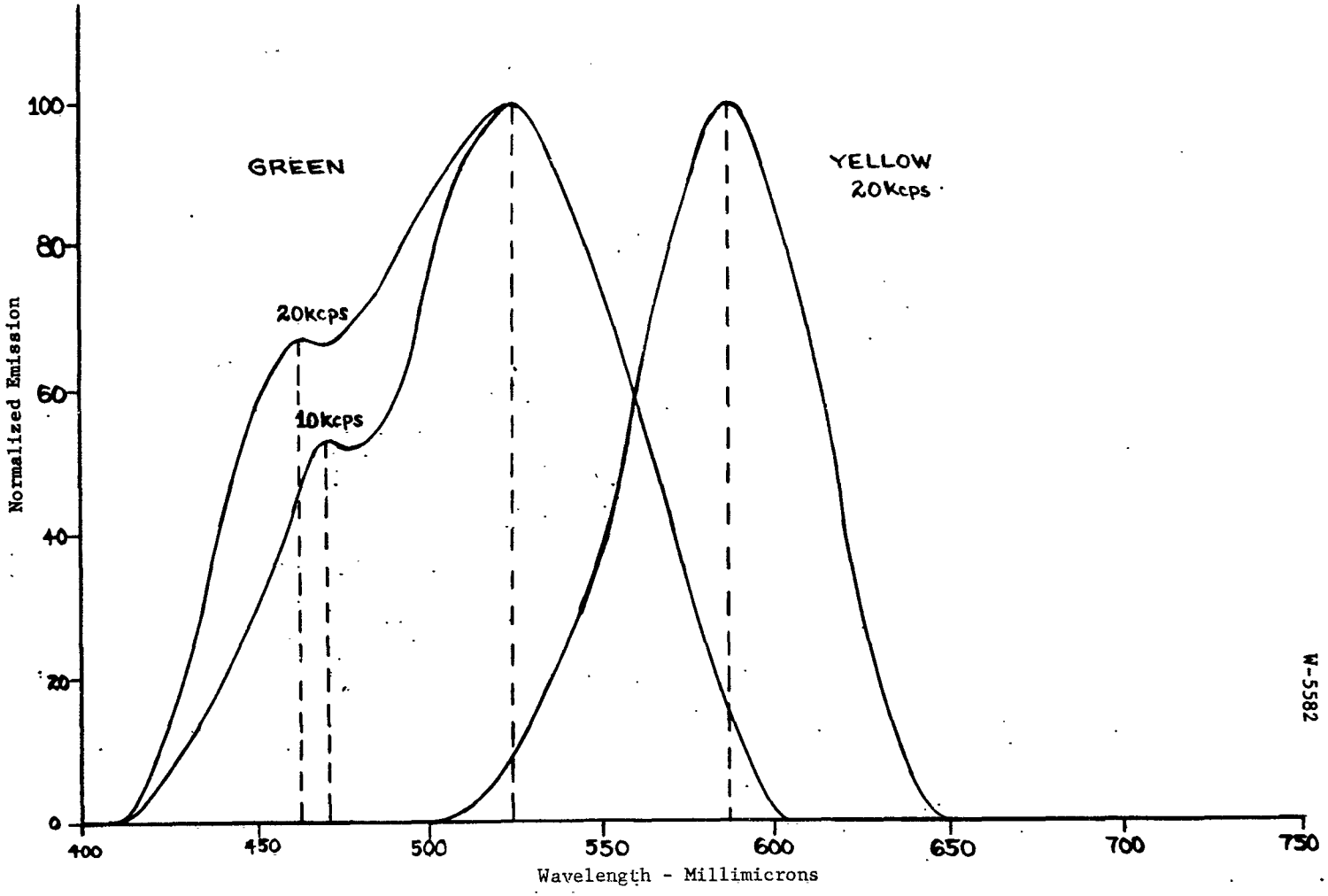


Figure 5

Spectral Distribution for green (ZnS:Cu,Pb,Cl) and yellow (ZnS:Mn:Cl) fil[illegible]

Hq. ESD, L.G. Hanscom Field, Bedford, Mass.
Rpt. No. ESD-TDR-63-169. SOME CHARACTERISTICS OF EVAPORATED ELECTROLUMINESCENT PHOSPHOR FILMS. Preliminary report, May 1963, 15p. incl. illus., 5 refs.

Unclassified Report

Vacuum deposited electroluminescent phosphor light sources have characteristics radically different from conventional electroluminescent panels.

1. Thin films
2. Phosphorescent materials
3. Luminescence
I. Project No. 708
II. Contract AF33 (600)-39852
III. The MITRE Corporation, Bedford, Mass.
IV. Hirsch, J.V.
V. W-5582

Hq. ESD, L.G. Hanscom Field, Bedford, Mass.
Rpt. No. ESD-TDR-63-169. SOME CHARACTERISTICS OF EVAPORATED ELECTROLUMINESCENT PHOSPHOR FILMS. Preliminary report, May 1963, 15p. incl. illus., 5 refs.

Unclassified Report

Vacuum deposited electroluminescent phosphor light sources have characteristics radically different from conventional electroluminescent panels.

1. Thin films
2. Phosphorescent materials
3. Luminescence
I. Project No. 708
II. Contract AF33 (600)-39852
III. The MITRE Corporation, Bedford, Mass.
IV. Hirsch, J.V.
V. W-5582

Hq. ESD, L.G. Hanscom Field, Bedford, Mass.
Rpt. No. ESD-TDR-63-169. SOME CHARACTERISTICS OF EVAPORATED ELECTROLUMINESCENT PHOSPHOR FILMS. Preliminary report, May 1963, 15p. incl. illus., 5 refs.

Unclassified Report

Vacuum deposited electroluminescent phosphor light sources have characteristics radically different from conventional electroluminescent panels.

1. Thin films
2. Phosphorescent materials
3. Luminescence
I. Project No. 708
II. Contract AF33 (600)-39852
III. The MITRE Corporation, Bedford, Mass.
IV. Hirsch, J.V.
V. W-5582

Hq. ESD, L.G. Hanscom Field, Bedford, Mass.
Rpt. No. ESD-TDR-63-169. SOME CHARACTERISTICS OF EVAPORATED ELECTROLUMINESCENT PHOSPHOR FILMS. Preliminary report, May 1963, 15p. incl. illus., 5 refs.

Unclassified Report

Vacuum deposited electroluminescent phosphor light sources have characteristics radically different from conventional electroluminescent panels.

1. Thin films
2. Phosphorescent materials
3. Luminescence
I. Project No. 708
II. Contract AF33 (600)-39852
III. The MITRE Corporation, Bedford, Mass.
IV. Hirsch, J.V.
V. W-5582

This paper describes the fabrication and some characteristics of films composed of yellow (ZnS:Mn;Cl) and green (ZnS:Cu,Pb;Cl) phosphors. Among the properties studied are brightness levels, spectral distribution and resistance and capacitance measurements.	VI. In ASTIA collection	This paper describes the fabrication and some characteristics of films composed of yellow (ZnS:Mn;Cl) and green (ZnS:Cu,Pb;Cl) phosphors. Among the properties studied are brightness levels, spectral distribution and resistance and capacitance measurements.	VI. In ASTIA collection
This paper describes the fabrication and some characteristics of films composed of yellow (ZnS:Mn;Cl) and green (ZnS:Cu,Pb;Cl) phosphors. Among the properties studied are brightness levels, spectral distribution and resistance and capacitance measurements.	VI. In ASTIA collection	This paper describes the fabrication and some characteristics of films composed of yellow (ZnS:Mn;Cl) and green (ZnS:Cu,Pb;Cl) phosphors. Among the properties studied are brightness levels, spectral distribution and resistance and capacitance measurements.	VI. In ASTIA collection